

1 TITLE OF THE INVENTION

Recording Liquid and Recording Method by Use
Thereof

5 BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to a recording liquid
to be used for various recording tools such as writing
implements, printers, etc. (hereinafter called an ink),
10 particularly an ink suitable for the ink jet recording
system in which recording is performed by permitting
liquid droplets to fly from an orifice of recording head
and also to a recording method by use thereof.

Description of the Related Art

15 The ink jet recording system has the advantages
of less noise generation during recording as well as
easy adaptation to color recording and capability of
giving recorded images of high resolution at high speed.
In the ink jet recording system, solutions of various
20 water-soluble dyes dissolved in water or mixtures
of water with organic solvents have been used as the
ink. In this case, the requisite characteristics of
the ink to be used are physical values of viscosity,
surface tension, etc., within appropriate ranges, high
25 dissolving stability of the dissolved components, no
clogging of minute orifices, capability of giving
recorded images with sufficiently high density, no

1 change in physical values or no precipitation of solid
components during storage, etc. Further, in addition to
the above characteristics, it is also required to have
the properties such that recording may be performed
5 without restriction with respect to the kind of recording
medium, that the fixing speed may be great, that the
recorded images may be excellent in light resistance, water
resistance, and solvent resistance (particularly alcohol
resistance), and also that recorded image with excellent
10 resolution may be given.

In the prior art, as the colorant of the ink in
the ink jet recording system, water-soluble dyes have been
primarily employed on account of the liquid medium being
aqueous and, by use of water-soluble dyes, many of the
15 above basic requirements for the ink jet recording system
have been satisfied. However, when water-soluble dyes are
used, since these water-solubles are inherently inferior
in light resistance, problems are frequently involved in
light resistance of the recorded images. More specifically,
20 when recorded images are exposed to the light from the
light sources such as sun light, fluorescent lamp or
projector, the recorded images may be extinguished, or
become less readable, or the image may be faded during
a prolonged term of storage. Accordingly, investigations
25 have been made regarding the addition of various additives
such as UV-absorbers or antioxidants for improvement of
light resistance with the basic characteristics maintained

1 as mentioned above for the ink for ink jet recording.

And, it has been expected to improve greatly light resistance of the recorded images by addition of such substances into an ink.

5 However, this kind of additive is inferior in solution stability in the liquid medium of ink particularly in solution stability in water, thus ensuing the problems that it precipitates as solid in the ink with lapse of time, or that it precipitates the dye by decomposing or
10 isomerizing the dye, thereby causing generation of clogging of nozzles.

 The ink jet recording method, although it has been said not to be particular as to paper and more easily adapted to plain paper as compared with other recording
15 methods, is not yet satisfactory under the present condition. More specifically, when printing is effected on plain paper commonly used in offices other than the paper for ink jet recording, such as notebooks, reporting paper, copying paper, letter paper, etc., the printed
20 ink will be spread along the fibers of the paper, whereby dot shape becomes unstable to generate so called feathering and therefore fine ruled lines, fine letters or complicated chinese characters become frequently unclear and difficult to see.

25 Further, since the papers as mentioned above are subjected to the treatment called "sizing" so that feathering may be retarded in letters written by a

1 writing implement with the use of an aqueous ink for
fountain pen, the ink cannot easily penetrate into the
paper in the printing conducted when by an ink jet
printer, resulting in poor drying characteristic at the
5 printed portion, whereby there are involved the problems
such that the printed letters are stained by smearing
with the cover of the printer and that the ink is
attached to the hand when the printed matter is touched
with a hand.

10 Accordingly, various improvements have been done
for the purpose of improving feathering and drying
characteristic of printed letters. For example, it has
been attempted to make the pH of the ink strongly
alkaline or to add a large amount of a surfactant in
15 the ink, etc. An ink having a pH of strongly alkaline
is dangerous when the ink is touched with hands and also
involves the drawbacks that it is not sometimes good in
both feathering and drying characteristic for papers
in which a certain kinds of sizing agents are employed.

20 On the other hand, addition of a large amount of a
surfactant causes such troubles that feathering occurred
remarkably depending on the paper, that the ink was not
ejected but retracted from the orifice face depending on
the conditions of the print head or contrariwise the
25 whole orifice face was wetted to give no ejection of
ink, etc.

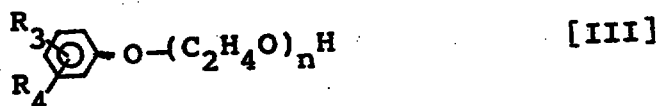
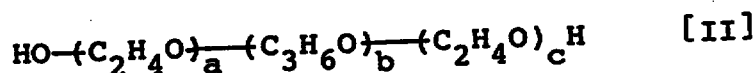
Although various improvements other than those

as described above have been hitherto attempted, under the present condition, no ink has been known which can solve all of the problems of aforesaid feathering and drying characteristic of printed letters.

SUMMARY OF THE INVENTION

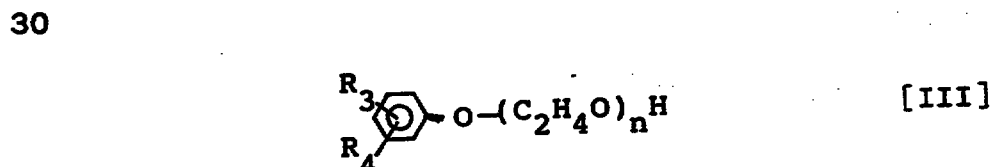
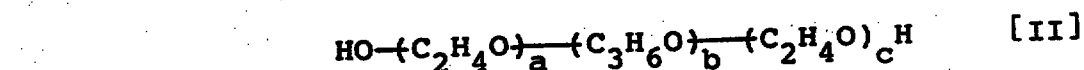
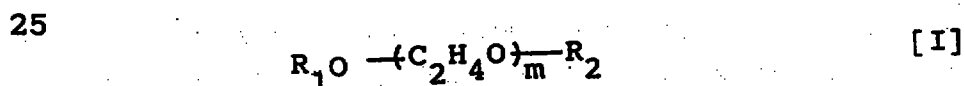
This invention provides an ink which is less prone to suffer from the above drawbacks and further provides a recording method in which the ink can be used. The ink may have excellent solution stability and contains a water-soluble dye. It may be useful for various writing implements and printers, particularly for ink jet recording, and may give images having excellent light resistance. The ink which may give an image of good printing quality and also may have good drying characteristics, without feathering or deformation of letters when printed on ordinary plain paper, etc. used in offices.

According to an aspect of the present invention, there is provided a recording liquid for ink-jet recording, comprising a water-soluble dye, water and at least one of the organic solvents represented by formulae (I), (II) or (III) below, wherein, if selected, said compound (I) is contained in said recording liquid within a range of 2 to 30% by weight, and said compounds (II) or (III), if selected, are contained in said recording liquid within a range of 6 to 30% by weight based on the total weight of the recording liquid:



(wherein R_1 and R_2 are each independently an alkyl group having 1 to 6 carbon atoms or an aryl group having 8 or less carbon atoms, m is an integer of 3 to 20, a and c are integers totalling not more than 78, b is an integer of 2 to 15, R_3 and R_4 are each independently a hydrogen atom or an alkyl group having 1 to 2 carbon atoms, and n is an integer of 4 to 20).

According to another aspect of the present invention, there is provided a recording method which performs recording by attaching liquid droplets of a recording liquid onto a recording medium, said recording medium being subjected to sizing and having fibers exposed on the surface of the recording medium, and said recording liquid comprising a water-soluble dye, water, and at least one of the organic solvents represented by formulae (I), (II) or (III) below, wherein, if selected, said compound (I) is contained in said recording liquid within a range of 2 to 30% by weight, and said compounds (II) or (III), if selected, are contained in said recording liquid within a range of 6 to 30% by weight based on the total weight of the recording liquid:



(wherein R_1 and R_2 are each independently an alkyl group having 1 to 6 carbon atoms or an aryl group having 8 or less carbon atoms, m is an integer of 3

to 20, a and c are integers totalling not more than 78, b is an integer of 2 to 15, R_3 and R_4 are each independently a hydrogen atom or an alkyl group having 1 to 2 carbon atoms, and n is an integer of 4 to 20).

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

To describe in more detail about the present invention, it has been practiced in the art to add a high boiling and water-soluble organic solvent such as polyhydric alcohols, etc., to an ink containing a water-soluble dye, particularly an ink for ink jet recording, in order to prevent ejecting nozzles, etc. from clogging by drying. When recording is effected on highly sized paper and the like, due to low liquid absorption of the paper, less volatile organic solvent will remain on the paper even if the water in the ink may be rapidly evaporated, and still the dye exists under dissolved state. Accordingly, there ensue the problems such that the head or fingers may be stained when touched with the printed paper and also that the printed letters may be disturbed.

1 On the other hand, in the case of a paper with
low degree of sizing having fibers exposed on the surface
such as the papers for office work, the organic solvent
will similarly remain even if the water may be evaporated
5 and also, since the dye is dissolved in the organic
solvent, the dye solution will be spread along the
fibers of the paper or into the voids between the fibers,
whereby, etc., impairing the quality of printed letter.

 Therefore, such an ink for ink jet recording
10 may ideally contain a dye in dissolved state when
residing within the instrument such as nozzles, etc.,
of the recording device, but will not easily give rise
to feathering by precipitation of the dye in the ink
from the ink medium, and various problems as mentioned
15 above were expected to be solved by use of such an ink.

 The present inventors have intensively studied
in order to obtain such an ideal ink, and consequently
found that by selecting and using an organic solvent
which can dissolve sufficiently a dye in a mixture of
20 water with an organic solvent and afford rapid precipi-
tation of the dye when the ratio of water is lowered by
evaporation of the water in the mixture on a recording
medium, there occurs no staining of other parts contacted
with the printed portion or disturbance of printed
25 letters even when printed on a paper with high degree of
sizing, because the dye in the ink can be rapidly
precipitated by evaporation of the water in the ink,

1 and also printing of high quality is possible on the
paper with low degree of sizing as the result of
rapid precipitation of the dye by similar evaporation of
the solvent, whereby only the liquid medium is feathered
5 into the paper without feathering of the dye.

Studies have been made about organic solvents
which can give such preferable results as mentioned
above, and it has been consequently found that the
above preferable effect, namely the effect that the dye
10 is maintained sufficiently under dissolved state before
evaporation of the water (within recording instrument or
nozzle) and the dye is readily precipitated by evapora-
tion of water (on paper), can be exhibited when the
solubility of a water-soluble dye in such an organic
15 solvent is 5 % by weight or less, and more preferably
4.5 % by weight or less.

The water-soluble dye in the ink to be used in
the present invention which first characterizes the
present invention may be those which are known per se,
20 including, for example, water-soluble dyes as represented
by direct dyes, acidic dyes, basic dyes, reactive dyes,
food grade dyes, etc. Examples of the dyes particularly
preferable for the inks in the ink jet recording
method and can satisfy the performances required such
25 as color forming characteristic, sharpness, stability,
light resistance and others may include:

direct dyes such as C.I. Direct Black 17, 19, 32,

1 51, 71, 108, 146, 154;

C.I. Direct Blue 6, 22, 25, 71, 86, 90, 106, 199;

C.I. Direct Red 1, 4, 17, 28, 83;

C.I. Direct Yellow 12, 24, 26, 86, 98, 142;

5 C.I. Direct Orange 34, 39, 44, 46, 60;

C.I. Direct Violet 47, 48;

C.I. Direct Brown 109;

C.I. Direct Green 59, and the like, acid dyes

such as

10 C.I. Acid Black 2, 7, 24, 26, 31, 52, 63, 112,
118;

C.I. Acid Blue 9, 22, 40, 59, 93, 102, 104, 113,
117, 120, 167, 229, 234;

C.I. Acid Red 1, 6, 32, 37, 51, 52, 80, 85, 87,

15 92, 94, 115, 180, 256, 317, 315;

C.I. Acid Yellow 11, 17, 23, 25, 29, 42, 61,
71;

C.I. Acid Orange 7, 19;

C.I. Acid Violet 49 and the like, and other dyes

20 such as

C.I. Basic Black 2;

C.I. Basic Blue 1, 3, 5, 7, 9, 24, 25, 26,
28, 29;

C.I. Basic Red 1, 2, 9, 12, 13, 14, 37;

25 C.I. Basic Violet 7, 14, 27;

C.I. Food Black 1, 2 and the like.

The above examples of dyes are particularly

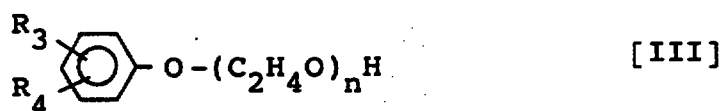
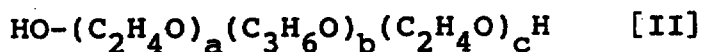
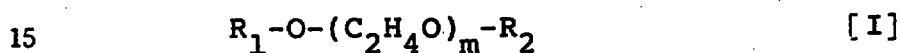
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1 preferred for the inks to be used in the present invention,
and the dyes to be used are not limited to these dyes.

Such a water-soluble dye is used at a proportion
generally of about 1 to 10 %, by weight more preferably
5 2 to 5 % by weight in the ink.

The solvent to be used for the ink is a
mixture of water with an organic solvent. As the water,
it is preferable to use deionized water instead of water
in general containing various kinds of ions.

10 The organic solvent to be used in admixture with
water has a boiling point under normal pressure of 120°C
or higher and is a compound represented by one of the
formulae shown below.



20

Typical examples of the compounds represented
by the formula [I] are shown in Table 1.

25

Table 1

	R_1	m	R_2
No. 1	CH_3	3	C_2H_5
2	C_2H_5	3	C_2H_5
3	C_3H_7	3	C_3H_7
4	C_4H_9	3	CH_3
5		3	CH_3
6	CH_3	4	CH_3
7	C_2H_5	4	C_2H_5
8	C_3H_7	4	C_3H_7
9	C_4H_9	4	CH_3
10	C_2H_5	5	C_2H_5
11	C_3H_7	5	C_3H_7
12	C_5H_{11}	5	CH_3
13	C_2H_5	6	C_2H_5
14	C_3H_7	6	C_2H_5
15	C_6H_{13}	6	CH_3
16	C_2H_5	7	CH_3
17	C_3H_7	7	CH_3
18	CH_3 — 	8	CH_3
19	C_3H_7	8	CH_3
20	C_4H_9	9	CH_3
21	C_2H_5	9	C_2H_5
22	C_4H_9	10	CH_3
23	CH_3	12	CH_3
24	C_3H_7	13	CH_3
25		15	CH_3
26	C_6H_{13}	17	CH_3
27	C_2H_5	18	CH_3
28	C_2H_5	19	C_2H_5
29	CH_3	20	CH_3

1 These compounds can be synthesized according to
the known methods.

 In the formula [I], R_1 and R_2 each independently
represent an alkyl group having 1 to 6 carbon atoms or
5 an aryl group having 8 or less carbon atoms, m is a
positive integer, 3 to 20.

 Particularly when m is within the range of from
3 to 20, the compounds of the formula [I] have low
vapor pressures, and hardly evaporated at around room
10 temperature to produce no sensible odor.

 Also, these compounds have no effect of preventing
clogging at the orifice tip, but contrariwise frequently
promote clogging. There is further the problem in
hygiene of working environment.

15 On the other hand, when m is 21 or more, the
viscosity of the ink will be markedly increased, whereby
there is the problem that fixing speed cannot be improved.

 In the formula [I], as the carbon chain of the
alkyl group is longer, the effect of penetrating into
20 paper becomes greater. However, if the carbon atoms
in the alkyl group are 7 or more, feathering becomes
extremely great similarly as in the case of a surfactant,

1 and it has been further found that its solubility in
an aqueous medium will be abruptly lowered with the
length of the carbon chain.

Therefore, the alkyl group should have
5 1 to 6 carbon atoms.

Also, the compound as a whole should
have 9 or more carbon atoms. The content of these
compounds is limited from the balance between the fixing
time of ink and feathering but the viscosity of the whole
10 ink can be controlled by varying the length of m.

The compound of the formula [I], which is a
diether, has more mild surface active ability as compared
with monoethers, whereby feathering is hardly caused
in the printed matter. Also, as compared with corresponding
15 polyoxyethylene, it is higher in vapor pressure but lower
in viscosity to be lowered in interface tension with
paper, and therefore it has the effect of increased
fixing speed of ink.

Next, the compounds represented by the formula
20 [II] are block copolymers of ethylene oxide (EO) and
propylene oxide (PO) of the $(EO)_a-(PO)_b$ type or $(EO)_a-$
 $(PO)_b-(EO)_c$ type, either of which can be obtained
according to the methods known in the art.

Of the block copolymers as defined above,
25 those which are useful for the object of the present
invention are those in which a and c, namely the
polymerization degree of EO is 78 or less, and b,

1 namely the polymerization degree of PO is 2 or more and
15 or less.

The above block copolymers particularly preferred
in the present invention are exemplified in terms of a,
5 b and c as shown in Table 2.

Table 2

	<u>No.</u>	<u>a</u>	<u>b</u>	<u>c</u>
	1	3	2	1
10	2	4	3	0
	3	6	3	0
	4	5	3	1
	5	2	4	0
	6	4	4	4
15	7	6	4	2
	8	8	4	0
	9	18	4	2
	10	4	5	0
	11	8	5	2
20	12	9	5	1
	13	8	6	4
	14	10	6	2
	15	12	7	2
	16	3	8	0
25	17	6	8	2
	18	7	8	1
	19	10	8	6

1	20	12	8	4
	21	14	8	2
	22	39	8	2
	23	16	9	2
5	24	19	10	1
	25	20	11	2
	26	11	12	1
	27	20	12	4
	28	22	12	2
10	29	20	14	8
	30	15	15	15

In the compounds represented by the above formula, if the sum of a and c exceeds 78, in spite of good compatibility with water, the compounds represented by the above formula have too high molecular weights, whereby the viscosity of ink becomes too high and, in spite of little feathering during printing, the drying and fixing speed of ink is low and, as the ink or ink jet recording, discharging characteristic of ink or the shape of ink dot becomes unstable. The same is the case if b is too small and, while if b is too large there is the fear that compatibility with water and drying and fixing speed of ink may become insufficient.

As to the weight ratio of EO in the molecule of the compound represented by the above formula, EO should preferably comprise 20 to 80 % by weight based

1 on the whole compound to accomplish best the object
of the present invention.

The compound represented by the formula [III]
is obtained by adding ethylene oxide to phenol or an
5 alkyl phenol having 1 or 2 alkyl group having 1 to 2
carbon atoms, and the method for producing it per se
may be similar to the method known in the art.

In the prior art, compounds prepared by adding
ethylene oxides to alkyl phenols have been known as
10 nonionic surfactants. However, such nonionic surfactants
of the prior art have generally 8 to 12 carbon atoms
in the alkyl group in order to control appropriately
their HLB values. Such nonionic surfactants have been
employed in the ink for ink jet of the prior art and
15 exhibit the action enhancing apparent drying and fixing
of ink, namely absorbability of ink into the recording
medium. However, when the recording medium is a paper
such as low sizing paper, excellent liquid absorbability
will contrariwise cause troubles to give rise to
20 excessive feathering of ink.

The present inventors have studied intensively
about such feathering of the ink for ink jet, and
consequently found that the problem of feathering
of ink as mentioned above can be solved and also
25 an ink capable of giving excellent drying and fixing
characteristic of ink even for high sizing paper can be
obtained by use of an ethylene oxide adduct of

1 alkylphenol as described above, in which the alkyl group on the phenol is eliminated or the alkyl group, if any, is made to have 1 to 2 carbon atoms, and the moles of ethylene oxide added are made 4 to 20.

5 Typical examples of preferable compounds of the above formula [III] to be used in the present invention are as shown below.

Table 3				
	Compound No.	R_3	R_4	n
10	1	Hydrogen atom	Hydrogen atom	4
	2	"	"	5
	3	"	"	6
	4	"	"	7
15	5	"	"	8
	6	"	"	10
	7	"	"	15
	8	"	"	20
	9	p-methyl	"	5
20	10	"	"	6
	11	"	"	7
	12	"	"	8
	13	"	"	10
	14	"	"	15
25	15	p-ethyl	"	6
	16	"	"	8
	17	"	"	10

1	18	p-ethyl	Hydrogen atom	12
	19	p-methyl	o-methyl	6
	20	"	"	8
	21	"	"	10
5	22	"	"	12
	23	p-ethyl	"	10
	24	"	"	10

As contrasted to the compounds [III] to be used in the present invention as described above, in the case of medium to high alkyl groups such as nonyl, octyl, dodecyl groups as in the nonionic surfactants of the prior art, the ink which contains such a nonionic surfactant is excellent in absorbability, but, in the case of a low sizing paper such as plain papers in general, excessive feathering of ink occurs to impair the quality of printing to a great extent. It has also been proposed to use an example in which the alkyl group is made to have 3 to 4 carbon atoms from the balance between drying and fixing characteristic of ink and feathering. However, even with an alkyl group having such carbon atoms, the problem of feathering for plain papers, etc., cannot be sufficiently solved, and it is impossible to avoid lowering in quality of printing.

On the other hand, as for the moles of ethylene oxide added (n), if n is made 3 or less, in spite of excellent effect of increased penetrating force of ink,

1 vapor pressure becomes higher to give less effect of
preventing clogging within the nozzle of the ink jet
recording device, and the compatibility with water
becomes insufficient, whereby clogging of the nozzle may
5 be sometimes recognized to be promoted. On the contrary,
if n is 21 or more, the viscosity of ink is increased
to make stable from the nozzle hardly achievable, and
also the drying and fixing speed after printing will be
very low. The amount of the compounds represented by
10 the above formulae [I] - [III] as described above
added in the ink is not particularly limited, but if
the ratio of the compound represented by the above
formulae in the ink is less than 0.5 % by weight, the
drying and fixing speed of ink becomes insufficient,
15 while if it exceeds 60 % by weight, the viscosity of
the ink may be excessively increased, and excessive
feathering of printed letters may occur or stability of
the ink may be lowered. Thus, the compound represented
by the above formulae should be contained in the ink
20 preferably at a proportion of 0.5 to 60 wt.%, more
preferably 0.5 to 30 wt.%.

Further, examples of water-soluble organic
solvents which may be contained in combination with
these compounds represented by the formulae [I] - [III]
25 may include alkyl alcohols having 1 to 4 carbon atoms
such as methyl alcohol, ethyl alcohol, n-propyl alcohol,
isopropyl alcohol, n-butyl alcohol, sec-butyl alcohol,

- 1 tert-butyl alcohol, isobutyl alcohol and the like;
amides such as dimethylformamide, dimethylacetamide and
the like; ketones or ketoalcohols such as acetone,
diacetone alcohol and the like; ethers such as
- 5 tetrahydrofuran, dioxane and the like; polyalkylene
glycols such as polyethylene glycol, polypropylene
glycol and the like; alkylene glycols having 2 to 6
carbon atoms such as ethylene glycol, propylene glycol,
butylene glycol, triethylene glycol, 1,2,6-hexanetriol,
- 10 thiodiglycol, hexylene glycol, diethylene glycol and
the like; glycerin; lower alkyl ethers of polyhydric
alcohols such as ethyleneglycol methyl (or ethyl) ether,
diethyleneglycol methyl(or ethyl) ether, triethyleneglycol
monomethyl(or ethyl) ether and the like; N-methyl-2-
- 15 pyrrolidone, 1,3-dimethyl-2-imidazolidinone, triethanolamine,
sulforane, etc. Of these water-soluble organic solvents,
polyhydric alcohols such as diethleneglycol, lower
alkyl ethers of polyhydric alcohols such as triethylene-
glycol monomethyl(or ethyl) ether are preferred.

The ink of the present invention can also
include, in addition to the above components, surfactants,
viscosity controllers, surface tension controllers,
etc., if necessary. Particularly, concerning surfactants,

1 since such surfactants as employed in the prior art
have great effect on feathering during printing, and
therefore should not be used in a large amount for the
object of the present invention and therefore their
5 amounts should be limited to, for example, 0.5 % by
weight or lower in the ink, preferably 0.4 % by weight
or lower and, more preferably 0.3 % by weight or lower.

The ink to be used in the present invention
comprises principally the above components, and the
10 principal specific feature of the ink to be used in the
present invention resides in that, in preparing the ink
comprising the above components, the combination of the
water-soluble dye used and the organic solvent used
is made a specific combination and also that the mixing
15 ratio of water and the organic solvent is made a specific
ratio. More specifically, while any of the water-
soluble dye and the organic solvent as described above
are useful, it is desirable that a water-soluble dye
should be selected so as to have a solubility of 5 %
20 by weight or less in at least one of the organic solvents
being used and is desirably present in the ink in the
amount specified above.

The solubility as herein mentioned of a water-
25 soluble dye in an organic solvent refers to grams of
the water-soluble dye dissolved in 100 g of the organic
solvent under normal pressure at 25 °C.

1 With such a specific feature, the ink to be used
in the present invention is sufficiently in a dissolved
state of the dye within the recording instrument or in
the nozzle, and the water-soluble dye after recording
5 comes out rapidly of the dissolved state with evapora-
tion of water to lose its fluidity. As the result, the
problems of poor drying or feathering of ink in various
recording medium can be also solved, and recorded images
of high quality and high resolution without feathering can
10 be formed not only on ink jet recording paper specially
prepared as a matter of course but also on plain papers
in general.

 The recoding medium which can be used in the
method of the present invention may include various
15 paper for ink jet recording proposed in large number in
the prior art or plastic sheets for OHP to enable
excellent recording as a matter of course, or otherwise
copying paper, reproting paper, bond paper, slip papers,
continuous business forms, printing paper for computer
20 may be all available, and the paper may be either low
sizing papers or high sizing papers.

 When a conventional ink, particularly an ink-
jet printing ink is used for printing on a plain paper
of a low sizing degree with the cellulose fiber exposed
25 on the recording surface, the feathering of the print will
be remarkable, making the high-quality printing impracti-
cable. In contrast, in the method of the present
invention, due to the effect of the ink as mentioned

1 above, no feathering of ink occurs even on such a plain
paper with low degree of sizing to give printing of high
quality. Thus, the method of the present invention is
still more suitable when employing such a paper with low
5 degree of sizing.

The present invention is particularly useful as the
ink jet recording method, and such an ink jet recording
method may be of any system, provided that it is a system
capable of imparting the ink onto a recording medium which
10 is the object to be ejected against by releasing effectively
the ink from a nozzle. Typical examples of such systems are
described in, for example, IEEE Transactions on Industry
Application, Vol. JA-13, No.1 (the February and March, 1977
issue) and the February 19, 1976 issue, the January 29, 1973
15 issue and the May 6, 1974 issue of Nikkei Electronics.
The systems described in these reports are suitable for
the present invention and, to explain some of them,
there is first the electrostatic attracting system.
This system includes the system in which recording is
20 effected by giving a strong electrical field between a
nozzle and an accelerating electrode placed several mm
ahead of the nozzle, thereby successively ejecting
particulated ink from the nozzle and giving information
signals to the deflecting electrodes while the ejected
25 inks fly between the deflecting electrodes, and also
the system in which ink particles are ejected in accord-
ance with the information signals without deflecting
the ink particles, and both are effective for the present

1 invention.

The second system is the system in which high pressure is applied on the ink by a small pump and minute ink particles are ejected forcibly by mechanical vibration of the nozzle by a quartz vibrator, etc., and the ink particles ejected are electrically charged corresponding to information signals simultaneously with ejection. The charged ink particles are deflected corresponding to the quantity of the charge during passage between the deflecting electrode plates. As another system utilizing this system, there is also the system called microdot ink jet system. According to this system, while the ink pressure and exciting conditions is maintained at adequate values within a certain ranges, two kinds of large and small ink droplets are generated from the nozzle tip, of which only the droplets with smaller sizes are utilized for recording. The specific feature of this system resides in that a group of minute liquid droplets can be obtained even with a thick nozzle apperture of the prior art.

The third system is the piezoelectric device system and, according to this system, a piezoelectric device is utilized in place of mechanical means such as pump in other systems as the means for pressurizing ink. This is the system, in which pressure is applied on the ink by the mechanical displacements created by giving electrical signals to the piezoelectric device, thereby

1 ejecting the ink from a nozzle.

It is also possible to use effectively the ink jet system as disclosed in Japanese Laid-open Patent Publication No. 59936/1979 in which the ink subjected
5 to the action of heat energy undergoes abrupt change in volume and the ink is ejected from the nozzle through the acting force by such a change in state.

The above examples show preferable recording methods of the present invention, and the present
10 invention is not limited to these recording methods, but it is of course useful for, for example, ink for use in other printers or writing implements.

The present invention is described in more detail by referring to the following examples, in which
15 parts and % are by weight.

Example 1

	Compound No. 2 in Table 1	7 parts
	Glycerin	5 parts
	Polyethylene glycol 400	5 parts
20	Ethylene glycol	10 parts
	C.I. Direct Black 154	5 parts
	Nonionic surfactant	0.1 parts
	[Emulgen PP-150 (trade mark), produced by Kao Sekken K.K.]	
25	Water	68 parts

(Solubility of C.I. Direct Black 154 in compound No. 2 in Table 1 being 3.5 %)

1 The above respective components were charged in
a vessel, stirred for 5 hours and the resultant mixture
was adjusted to pH 7.5 with 0.1 % aqueous sodium
hydroxide.

5 Next, the mixture was filtered and a pressuriza-
tion through Fluoropore filter [trade mark; produced by
Sumitomo Denko K.K.] with a pore size of 0.45 μ m to obtain
a recording liquid A of the present invention. The
physical properties, solubility and odor of the recording
10 liquid A obtained were evaluated. The results are shown
in Table 4.

The above recording liquid A was mounted on an
ink jet printer (trially made machine produced by
Canon K.K.) which performs recording by utilization
15 of heat energy and printing was effected on continuous
business forms and copying paper, and the recording
characteristics with respective fixing characteristic
and feathering were evaluated.

Further, the machine was left to stand for 5
20 minutes without capping the printing head, and thereafter
printing operation was again performed.

After 3 lines of printing was conducted, the
power source of the printer was turned off and clogging
of 24 nozzles was examined. The results are shown in
25 Table 5.

Examples 2 - 6

Recording liquid B

1	Compound No. 4 in Table 1	4 parts
	Triethylene glycol	5 parts
(2)	Diethylene glycol	10 parts
	C.I. Food Black 2	6 parts
5	Water	75 parts

(Solubility of C.I. Food Black 2 in Compound
No. 4 in Table 1 being 1 % or less)

Recording liquid C

	Compound No. 11 in Table 1	3 parts
10	N-methyl-2-pyrrolidone	10 parts
	Polyethylene glycol	15 parts
	Hexylene glycol	2 parts
(3)	Anionic surfactant	0.1 parts
	[Caribon B (trade mark), produced by Sanyo Kasei K.K.]	
15	C.I. Acid Red 8	4 parts
	Water	66 parts

(Solubility of C.I. Acid Red 8 in Compound
No. 11 in Table 1 being 1 % or less)

20 Recording liquid D

	Compound No. 17 in Table 1	20 parts
	Ethylene glycol	10 parts
	Nonionic surfactant	0.05 parts
(4)	[Nissan nonion K211 (trade mark), produced by Nippon Yushi K.K.]	
25	C.I. Direct Blue 86	4 parts
	Water	66 parts

- 1 (solubility of C.I. Direct Blue 86 in compound
No. 17 in Table 1 being 1.5 %)

Recording liquid E

- 5 (5) { Compound No. 21 in Table 1 30 parts
C.I. Direct Blue 199 5 parts
Water 65 parts
(Solubility of C.I. Direct Blue 199 in Compound
No. 22 in Table 1 being 3.5 %)

Recording liquid F

- 10 { Compound No. 26 in Table 1 2 parts
Compound No. 5 in Table 1 5 parts
Glycerin 10 parts
(6) { Ethyleneglycol 10 parts
C.I. Direct Yellow 86 2 parts
15 { C.I. Acid Yellow 23 2 parts
Water 69 parts
(Solubility of C.I. Acid Yellow 23 in Compound
No. 5 in Table 1 being 1 % or less)

Example 1 was repeated except for using the
20 above recording liquids B - F in place of the recording
liquid A in Example 1, and the recording liquids and
recording characteristics were evaluated. The results
are shown in Table 4 and Table 5.

1

Table 4

5

10

15

Examples: Recording liquid	Surface tension (dyne/cm)	Viscosity (C.P.)	Solubility ^{*1}	Odor ^{*2}
(A)	47.2	2.8	○	○
(B)	50.2	2.0	○	○
(C)	46.1	3.4	○	○
(D)	42.5	2.3	○	○
(E)	53.4	2.5	○	○
(F)	54.7	2.4	○	○

20

***1 Evaluation standards**

- o Ink completely homogenized.
- x Separation of oily substance
recognized.

25

***2 Evaluation standards**

- o ... Odorless or substantially insensible.
- x ... Unpleasant feeling felt in office or
home.

Table 5

Examples: recording liquid	Fixing ^{*3} characteristic		Feathering ^{*4} ratio		^{*5} Clogging
	Fanfold paper	Copying paper	Fanfold paper	Copying paper	
(A)	○	◎	○	○	0
(B)	◎	◎	○	○	0
(C)	○	◎	○	○	1
(D)	◎	◎	○	○	1
(E)	◎	◎	○	○	0
(F)	◎	◎	○	○	0

^{*3} 10 seconds, 30 seconds after printing, the printed portion was rubbed with a filter paper (trade mark; No. 5C, produced by Toyo Kagaku Sangyo K.K.).

- 1 ⊙ ... No smearing after 10 seconds
 ○ ... Slight smearing after 10 seconds
 △ ... Slight smearing after 30 seconds
 X ... Considerable smearing after 30 seconds

5 *4 The number of dots with feathering in 300
printed dots was evaluated in terms of percent.

- ... Less than 10 % of feathering
 △ ... 10 % to less than 20 % of feathering
 X ... 20 % or more of feathering

10 *5 Number of nozzles causing clogging out of 24
nozzles.

For inks (C) and (D), clogging was cancelled
by performing restoration operation.

Examples 7 - 11

15 The components shown below were stirred for 5
hours, and the resulting mixture was adjusted to pH
7.5 with a 0.1 % aqueous sodium hydroxide and further
filtered under pressurization through a membrane filter
with a pore size of 0.45 μ (trade name, Fluoropore
20 filter, produced by Sumitomo Denko K.K.) to provide
the ink of the present invention.

Recording liquid G

25	(7) {	Compound No. 21 in Table 2	15 parts
		C.I. Direct Black 154	5 parts
		Water	80 parts

(Solubility of C.I. Direct Black 154 in Compound
No. 21 in Table 2 being 2 %)

1 Recording liquid H

5	(8)	Compound No. 6 in Table 2	20 parts
		Compound No. 7 in Table 2	10 parts
		Glycerin	5 parts
		C.I. Food Black 2	4 parts
		Water	61 parts

(Solubility of C.I. Food Black 2 in Compound No. 6 and 7 in Table 2 being 1 % or less, and 1 % or less, respectively)

10 Recording liquid I

15	(9)	Compound No. 27 in Table 2	8 parts
		Glycerin	3 parts
		Tetraethylene glycol	5 parts
		Ethylene glycol	15 parts
		C.I. Acid Blue 254	3 parts
		Water	66 parts

(Solubility of C.I. Acid Blue 254 in Compound No. 27 in Table 2 being 1.5 %)

Recording liquid J

20	(10)	Compound No. 22 in Table 2	20 parts
		Triethylene glycol dimethyl ether	10 parts
		Nonionic surfactant (trade name: Surfinol 104 produced by Nisshin Kogyo K.K.)	0.1 parts
		Reactive dye (trade name: Kayaseron React Red CN-3B produced by Nippon Kayaku K.K.)	4 parts
		Water	66 parts

1 (Solubility of Reaction dye in Compound

No. 22 in Table 2 being 3.5 %)

Recording liquid K

5	(11)	Compound No. 20 in Table 2	6 parts
		Glycerin	5 parts
		Polyethyleneglycol 300	10 parts
		C.I. Direct Yellow 86	2 parts
		C.I. Acid Yellow 23	2 parts
		Water	75 parts

10 (Solubility of C.I. Direct Yellow 86, C.I. Acid Yellow 23 in compound No. 20 in Table 2 being 2 %, 1 % or less)

Recording was performed in the same manner as Example 1 except for using the recording liquids G - J in place of the recording liquid A in Example 1, and the recording characteristics were evaluated. The results are shown in Tables 6 and 7.

Table 6

20	Ink		Surface tension (dyne/cm)	Viscosity (C.P.)	Solubility
	Recording liquid				
	G		43.4	3.1	○
	"	H	48.3	3.3	○
	"	I	45.2	2.9	○
25	"	J	33.6	3.5	○
	"	K	43.4	3.1	○

1

Table 7

	Ink	Example				
		7	8	9	10	11
5	<u>Discharging stability *6</u>	○	○	○	○	○
	<u>Fixing characteristic *3</u>					
10	Continuous slip paper	◎	○	◎	○	○
	Copying paper	◎	◎	◎	◎	◎
	<u>Feathering *4</u>					
15	Continuous slip paper	○	○	○	○	○
	Copying paper	○	○	○	○	○
20	<u>Clogging *5</u>	0	1	0	1	0

Examples 12 - 16

The components shown below were stirred for 5 hours, and the resulting mixture was adjusted to pH 7.5 with a 0.1 % aqueous sodium hydroxide and further filtered under pressurization through a membrane filter with a pore size of 0.45 μ (trade name, Fluoropore filter,

1 produced by Sumitomo Denko K.K.) to provide the ink
of the present invention.

Recording liquid L

5	(12)	Compound No. 6 in Table 3	20 parts
		C.I. Direct Black 154	5 parts
		Water	75 parts

(Solubility of C.I. Direct Black in Compound
No. 6 in Table 3 being 4.5 %)

Recording liquid M

10	(13)	Compound No. 3 in Table 3	20 parts
		Compound No. 7 in Table 3	10 parts
		Glycerin	5 parts
		C.I. Food Black 2	4 parts
		Water	61 parts

15 (Solubility of C.I. Food Black in Compound
No. 3, No. 7 in Table 3 being 3 %, 4.5 %, respectively)

Recording liquid N

20	(14)	Compound No. 10 in Table 3	8 parts
		Glycerin	3 parts
		Tetraethylene glycol	5 parts
		Ethylene glycol	15 parts
		C.I. Acid Blue 254	3 parts
		Water	66 parts

(Solubility of C.I. Acid Red 254 in compound
25 No. 10 in Table 3 being 1 %)

Recording liquid O

1	{	Compound No. 21 in Table 3	20 parts
		Triethylene glycol dimethyl ether	10 parts
		Nonionic surfactant (trade name:	
(15)		Surfinol 104 produced by Nisshin Kagaku	
5		Kogyo K.K.)	0.1 parts
		C.I. Reactive Red 221	4 parts
		Water	66 parts

(Solubility of C.I. Reactive Red 221 in compound No. 21 in Table 3 being 1 %)

10 Recording liquid P

	{	Compound No. 2 in Table 3	6 parts
		Glycerin	5 parts
(16)		Polyethyleneglycol 300	10 parts
		C.I. Direct Yellow 86	2 parts
15		C.I. Acid Yellow 23	2 parts
		Water	75 parts

(Solubility of C.I. Direct Yellow 23, C.I. Acid Yellow 23 in Compound No. 2 in Table 3 being 4.5 %, 2 %, respectively)

20 Recording was performed in the same manner as Example 1 except for using the recording liquids L - P in place of the recording liquid A in Example 1, and the recording characteristics were evaluated. The results are shown in Tables 8 and 9.

Table 8

Ink	Surface tension (dyne/cm)	Viscosity (C.P.)	Solubility
Recording liquid L	43.6	2.8	○
" M	41.0	3.5	○
" N	46.3	2.5	○
" O	33.6	2.5	○
" P	52.4	2.3	○

Table 9

Ink	Example					
	12	13	14	15	16	6
<u>Discharging stability #6</u>	○	○	○	○	○	X
<u>Fixing characteristic #3</u>						
Continuous business form	◎	○	◎	○	○	X
Copying paper	◎	◎	◎	◎	◎	△
<u>Feathering #4</u>						
Continuous business form	○	○	○	○	○	○
Copying paper	○	○	○	○	○	○
<u>Clogging #5</u>	0	0	0	1	1	10

The evaluation standard for the discharge stability *6
is:

Discharge Stability:

5

The dot constitution at the portion of the printer
alphabet letters are observed through a magnifying
class.

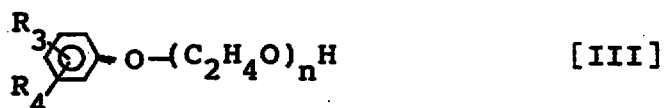
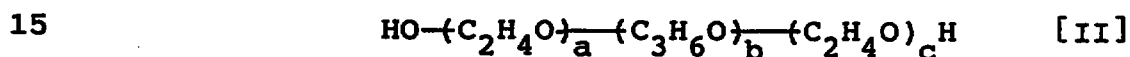
10

O....no disturbance observed in dot constitution.

X....disturbance observed or satellite dots occurred.

CLAIMS

1. An aqueous recording liquid for ink-jet recording, comprising a water-soluble dye, water and at least one of the organic solvents represented by formulae (I), (II) or (III) below, wherein, if selected, said compound (I) is contained in said recording liquid within a range of 2 to 30% by weight, and said compounds (II) or (III), if selected, are contained in said recording liquid within a range of 6 to 30% by weight based on the total weight of the recording liquid:



(wherein R_1 and R_2 are each independently an alkyl group having 1 to 6 carbon atoms or an aryl group having 8 or less carbon atoms, m is an integer of 3 to 20, a and c are integers totalling not more than 78, b is an integer of 2 to 15, R_3 and R_4 are each independently a hydrogen atom or an alkyl group having



1 to 2 carbon atoms, and n is an integer of 4 to 20).

2. A recording liquid according to claim 1, wherein
5 said compound has a boiling point of 120°C or higher.

3. A recording liquid according to claim 1 or 2,
wherein the content of water is within the range of
10 from 61 to 80% by weight based on the total weight of the recording liquid.

4. A recording liquid according to claim 1, 2 or 3,
wherein the recording liquid further contains a
15 water-soluble organic solvent selected from the group of alkyl alcohols having 1 to 4 carbon atoms, amides, ketones, polyalkylene glycols, alkylene glycols having 2 to 6 carbon atoms, lower alkyl ethers of polyhydric alcohols, N-methyl-2-pyrrolidone and 1,3-dimethyl-2-imidazolidinone.
20

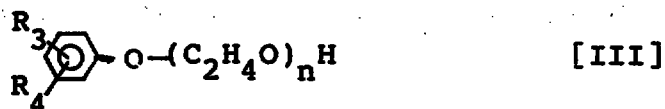
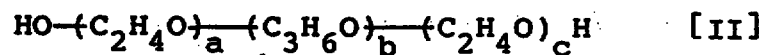
5. A recording liquid according to any preceding claim wherein the water soluble dye has a solubility of 5% by weight or less in said organic solvent.
25



6. A recording liquid according to claim 5, wherein said water-soluble dye has a solubility of 4.5% by weight or less in the organic solvent.

5 7. A recording method which performs recording by
attaching liquid droplets of a recording liquid onto a
recording medium, said recording medium being
subjected to sizing and having fibers exposed on the
surface of the recording medium, and said recording
10 liquid comprising a water-soluble dye, water, and at
least one of the organic solvents represented by
formulae (I), (II) or (III) below, wherein, if
selected, said compound (I) is contained in said
recording liquid within a range of 2 to 30% by weight,
15 and said compounds (II) or (III), if selected, are
contained in said recording liquid within a range of 6
to 30% by weight based on the total weight of the
recording liquid:

20



(wherein R_1 and R_2 are each independently an alkyl group having 1 to 6 carbon atoms or an aryl group having 8 or less carbon atoms, m is an integer of 3 to 20, a and c are integers totalling not more than 78, b is an integer of 2 to 15, R_3 and R_4 are each independently a hydrogen atom or an alkyl group having 1 to 2 carbon atoms, and n is an integer of 4 to 20).

8. A recording method according to claim 7, wherein the content of water is within the range of from 61 to 80% by weight based on the total weight of the recording liquid.

9. A recording method according to claim 7, wherein said recording medium is low sizing paper.



10. A recording liquid according to claim 6 or 9 wherein the said compounds represented by the formula I comprise those specified in Table 1.

5 11. A recording liquid according to claim 6 or 9 wherein the said compounds represented by the formula II comprise those specified in Table 2.

10 12. A recording liquid according to claim 6 or 9 wherein the said compounds represented by the Formula III comprise those specified in Table 3.

13. A recording liquid according to claim 1 and substantially as hereinbefore described.

15

14. A recording liquid substantially as hereinbefore described with reference to any one of Examples 1 to 16.

20 15. A recording method according to claim 7 and substantially as hereinbefore described.

16. A recording method substantially as hereinbefore described with reference to Examples 1 to
25 16.



* C L M S *